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Observation of hysteretic magnetic phase transitions coupled with orientation motion of ions and dielectric relaxation in a one-dimensional nickel-bis-dithiolene molecule solid

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Experimental details:

Preparation sample of [4'-CF_3bzPy][Ni(mnt)$_2$] (1)[1]. A MeOH solution (10 cm^3) of I_2 (205 mg, 0.80 mmol) was slowly added to a MeCN solution (25 cm^3) of [4'-CF_3bzPy]$_2$[Ni(mnt)$_2$] (573 mg, 1.0 mmol), the mixture was allowed standing overnight after stirred for 30 min. The dark powder formed were filtered off, washed with MeOH and dried in vacuum. Yield ~65%. Anal. Calc. for $C_{21}H_{11}F_3N_5NiS_4$: C, 43.69; H, 1.92; N, 12.13%. Found: C, 43.73; H, 2.09; N, 12.15%. Infrared (IR) spectrum (KBr pellet, cm^{-1}) and the assignments for the listed bands: [2, 3] 3139(w), 3094(w) and 3070(w) attributed to the ν_{C-H} of the phenyl ring; 2207(vs) and 2153(sh) assigned to the $\nu_{C\equiv N}$ of the mnt^{2-} ligands; 1633(s) 1486(vs), and 1418(s) attributed to the ring stretching vibration of the pyridyl and phenyl rings in the cation; 1450(s) arose from the $\nu_{C=C}$ of the mnt^{2-} ligands; 1121(s) assigned to ν_{C-F} of CF_3; 1159(vs) and 1068(m) arose from the ν_{C-S} + ν_{C-C} of mnt^{2-} ligands;751(m), 681(m), 502(s) for π_{C-CN} and 801(m) attributed to ν_{C-S} of mnt^{2-} ligands.

β-crystals of **1** suitable for single crystal x-ray diffraction can be obtained by slow evaporation of the saturated acetonitrile or acetone solution of the above powdered sample with a little amount of isopropanol at ambient temperature for 5-7 days.

Reference:

[1] H. B. Duan, X. R. Chen, H. Yang, X. M. Ren, F. Xuan, S. M. Zhou, *Inorg. Chem.* **2013**, *52*, 3870-3877.

[2] C. W. Schläpfer, K. Nakamoto, *Inorg. Chem.* **1975**, 14, 1338-1344.

[3] C. B. Martin , B. O. Patrick , A. C.Goodwin, *J. Org. Chem.*, **1999**, *64*, 7807–7812

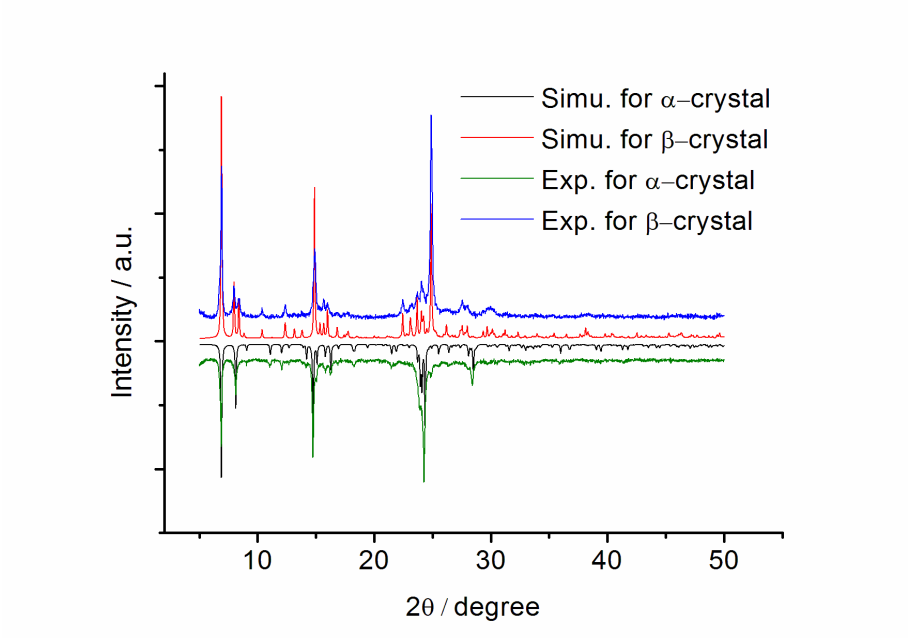


Figure S1 Experimental and simulated PXRD patterns of **α**-Crystal and **β**-Crystal at room temperature.

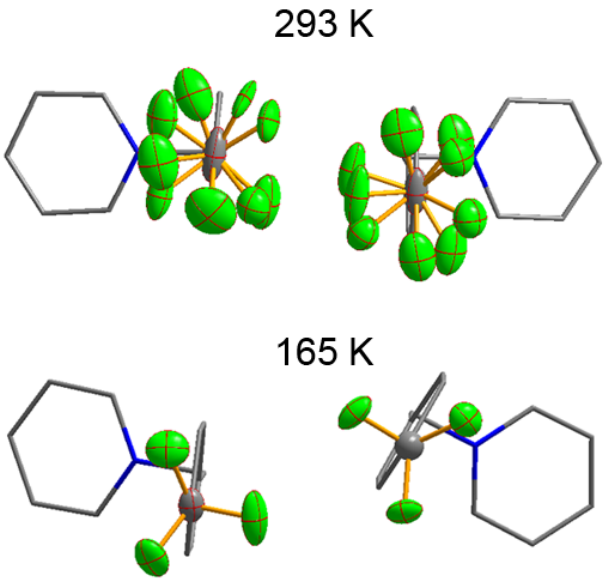


Figure S2 CF_3 groups are structurally disordered with two possible sites for each Fluorine atom at 293 K, while ordered at 165 K.

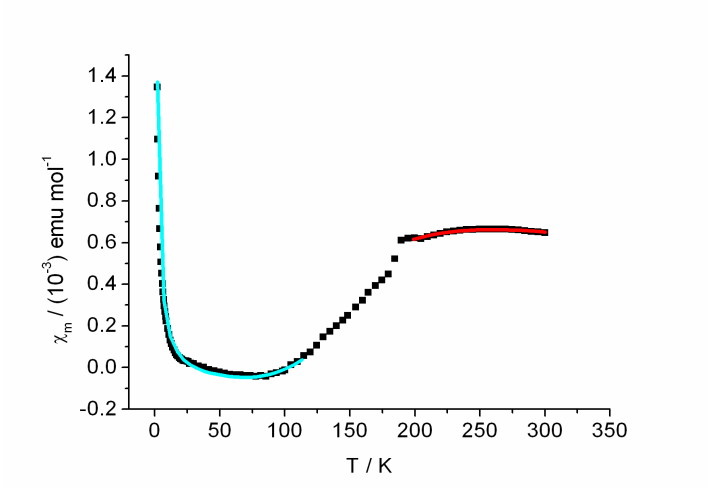
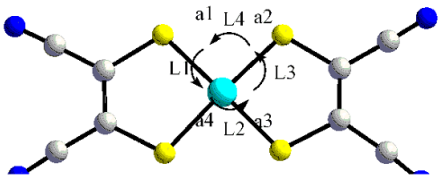


Figure S3 Magnetic susceptibility in the form χ_m-T for **β-crystal** measured in cooling model (Solid squares: experimental data; cyan line: fit using the equation $\chi_m = \alpha \cdot \exp(-Ea/k_B T)/T^{0.5} + C/(T-\theta) + \chi_0$ to give C= 0.00294(5) emu K mol^{-1}, θ = -0.01(4) K and χ_0 = -0.00009(7) emu mol^{-1}.

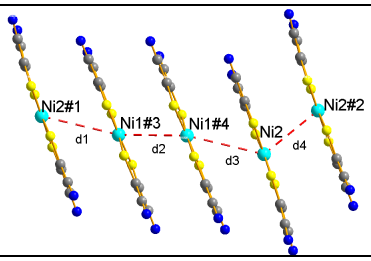
Table S1: Characteristic bond lengths and angles in $[Ni(mnt)_2]^-$ moiety of β-Crystal at selected temperature



	293 K*	**293 K****	**250 K***	**250 K****	**220 K***	**220 K****
a1 / Å	2.133(2)	2.140(2)	2.1359(13)	2.1485(13)	2.1338(12)	2.1467(12)
a2 / Å	2.146(2)	2.148(2)	2.1483(13)	2.1484(13)	2.1489(13)	2.1483(13)
a3 / Å	2.1514(19)	2.139(2)	2.1539(12)	2.1489(12)	2.1487(12)	2.1457(12)
a4 / Å	2.145(2)	2.143(2)	2.1493(13)	2.1425(13)	2.1464(12)	2.1372(13)
∠1 / °	92.28(8)	92.16(9)	92.35(5)	92.25(5)	92.26(5)	92.28(5)
∠2 / °	88.94(7)	86.40(8)	88.89(5)	86.42(5)	89.04(5)	86.46(5)
∠3 / °	92.76(8)	92.63(8)	92.76(5)	92.67(5)	92.68(5)	92.69(5)
∠4 / °	86.02(8)	88.87(9)	86.01(5)	88.73(5)	86.02(5)	88.63(5)
	165 K*	**165 K****	**145 K***	**145 K****	**125 K***	**125 K****
a1 / Å	2.1486(7)	2.1542(7)	2.1478(6)	2.1561(6)	2.1494(11)	2.1590(10)
a2 / Å	2.1532(7)	2.1559(7)	2.1529(7)	2.1548(7)	2.1596(10)	2.1598(10)
a3 / Å	2.1323(7)	2.1503(7)	2.1341(6)	2.1391(6)	2.1341(11)	2.1396(11)
a4 / Å	2.1491(7)	2.1381(7)	2.1498(7)	2.1503(7)	2.1561(10)	2.1549(10)
∠1 / °	92.86(3)	92.31(3)	92.80(2)	92.69(2)	92.95(4)	92.81(4)
∠2 / °	86.17(3)	85.89(3)	86.13(2)	85.95(2)	85.93(4)	85.84(4)
∠3 / °	92.31(3)	92.72(3)	92.28(3)	92.23(2)	92.42(4)	92.35(4)
∠4 / °	88.72(3)	89.10(3)	88.84(3)	89.15(2)	88.75(4)	89.03(4)
	100 K*	**100 K****				
a1 / Å	2.153(3)	2.134(3)				
a2 / Å	2.151(3)	2.147(3)				
a3 / Å	2.140(3)	2.146(3)				
a4 / Å	2.149(3)	2.152(3)				
∠1 / °	92.80(12)	92.24(12)				
∠2 / °	85.83(12)	88.99(12)				
∠3 / °	92.35(12)	92.74(12)				
∠4 / °	89.04(12)	86.08(12)				

Noted: There are two crystallographic in-equivalent anions in the crystal structure of β-crystal. The symbols *and** represent the Ni(1) and Ni(2) anions, respectively.

Table S2: The selected interatomic separations of in the β-crystal at different temperatures



Temperature	d1 /Å Ni1#3-Ni2#1	d2/Å Ni1#3-Ni1#4	d3 /Å Ni1#4-Ni2	d4 /Å Ni2-Ni2#2
293 K	4.487	4.038	4.487	4.029
250 K	4.473	4.016	4.473	4.003
220 K	4.466	3.999	4.466	3.997
165 K	4.495	4.008	4.495	3.918
145 K	4.489	4.007	4.489	3.906
125 K	4.481	4.002	4.481	3.892
100 K	4.479	4.002	4.479	3.877

Symmetry code : #1 –x, -y, 1-z ; #2 –x, -y, -z ; #3 1-x, -y, 1-z ; #4 -1+x, y, z

Table S3: Characteristic dihedral angles in the cation of β-crystal, where θ_1, θ_2 and θ_3 represent the dihedral angle between the pyridyl ring, phenyl ring and the reference plane (C_{phenyl}-CH_2-$N_{pyridyl}$) as well as between the pyridyl and phenyl rings

Temperature	θ1 /°	θ2 /°	θ3 /°
293 K*	87.2	89.8	69.6
293 K**	82.2	84.5	67.7
250 K*	88.4	88.3	69.4
250 K**	81.7	86.0	72.1
220 K*	88.6	87.7	69.7
220 K**	82.7	85.9	71.7
165 K*	88.3	88.2	70.8
165 K**	89.8	88.6	66.6
145 K*	88.3	88.5	70.8
145 K**	89.6	88.5	66.3
125 K*	87.0	89.0	71.2
125 K**	89.9	88.8	70.0
100 K*	89.3	89.1	66.6
100 K**	87.7	87.8	71.3

* and **: Two types of crystallographically independent cations in the structure of β-crystal phase at 293, 250, 220, 165, 145,125 and 100 K.